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Thermodynamic comparison of molecular recognition of vaporous guests by solid calixarene and diol hosts

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Abstract

Molecular recognition of vaporous guests by the solid hosts 2,2′-bis(9-hydroxyfluore--9-yl)biphenyl (1) and tert-butylcalix[4]arene (2) was studied. For this purpose the vapour sorption isotherms of 15 organic compounds with various molecular size and group composition with the solid hosts 1 and 2 were determined by static gas chromatographic headspace analysis. Most of the isotherms obtained show a definite inclusion threshold at a specific guest activity and a saturation part corresponding to the corresponding to the formation of stoichiometric supramolecular compounds. The stoichiometry of the host-guest compounds and free energies of their formation based on different standard states were determined. The free energy of guest transfer from the standard state of an infinitely dilute guest solution in toluene to the solid inclusion compound was assumed to be a molecular recognition parameter in the systems studied. For host 1 this transfer free energy exhibits a reasonably good 2-parameter correlation with guest molar refraction and free energy of H-bonding between guest and alcohols. Bad correlation was obtained for solid host 2. The effect of the guest structural parameters on molecular recognition by hosts 1 and 2 is discussed in terms of the different size of potential cavities in the host crystals and different ability of the hosts to H-bond with guests.